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Electrical transport properties of $LaXO_{3+\delta}$ (X = Mn, Co, Ni)

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Abstract : We report here the resistivity (1 8 K < T < 300 K) and magnetoresistanoe (0 < H < 7 Tesla) measurement of perovskite oxides $LaMnO_{3+\delta}$, $LaCoO_{3+\delta}$ and $LaNiO_{3+\delta}$. The sample $LaMnO_{3+\delta}$ shows a small increase in resistivity in the low temperature range below 30 K. It also shows a large resistivity peak and large negative magnetoresistance in the temperature range about 250 K which can be ascribed to the double exchange mechanism due to the presence of mixed valency of manganese (Mn^{3+}/Mn^{4+}) in this compound The $LaCoO_{3+\delta}$ sample shows a sharp fall in the resistivity near 50 K and after that a semiconducting behaviour which is due to the combined effect of spin state transition of the Co ion and the typical thermal activation of the semiconductors. The $LaNiO_{3+\delta}$ sample shows a metal to semiconducting type of transition near 135 K which shifts towards higher temperature with the application of magnetic field

Keywords : Perovskite oxides, resistivity, magnetoresistance.

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1. Introduction

The perovskite oxide has been a subject of enormous importance due to its anomalous electrical and magnetic properties [1–3]. Among them, $LaMnO_3$ has been extensively studied due to the occurrence of very large negative magnetoresistance when some Lanthanum ions are substituted with divalent cations such as Ca, Ba, Sr, Pb [4–7]. It has been found that $LaCoO_3$ and $LaNiO_3$ also have some effect on this divalent cation substitution. Various conduction mechanisms and a variety of cation valence and spin state distributions have been tried to explain these properties. Among them the double exchange interaction model is a popular one to interpret the origin of both ferromagnetism and metallic behaviour. However, the origin of GMR remains to be clarified. Later it has been found that the occurrence of GMR has some close relation with other physical properties like magnetisation [8], Jahn-Teller effect [9] and magnetic field induced first order phase

transition [10]. For $LaCoO_3$ a semiemperical model suggested by Sehlin *et al* [11] in which the population of small polarons is allowed to change as a function of temperature *via* the mechanism of charge disproportionation. The energy required for polaron formation by this mechanism is modelled as screened by a coulomb interaction with nearby small polarons. The charge carrier site occupancies generated by this model successfully interpreted the electrical conductivity and Seebeck coefficient for $La_{1-x}Ca_xCoO_3$. $LaNiO_3$ on the other hand, has shown a metallic behaviour with linear temperature dependence at high temperature and $T^{1/2}$ dependence at low temperature below 50 K. However, the dependence of electrical resistivity and magnetoresistance for these samples on oxygen stoichiometry has not been studied in detail. The occurrence of mixed valency of the transition metal, which is responsible for this anomalous electrical and magnetic properties can also be controlled by changing oxygen stoichiometry. In this work, we have studied the electrical resistivity and magnetoresistance of $LaXO_{3+\delta}$ (X = Mn, Co, Ni) in the temperature range 1.8 K–300 K and magnetic field range 0–7 Tesla.

2. Experimental

All the three samples were prepared by standard ceramic method. La_2O_3 (99.9%) and $MnCO_3$ (99.9%) were taken in the stoichiometric ratio for preparing $LaMnO_3$ and they were then mixed together with ethanol. The mixture was then dried and grinded to get a homogeneous mixture and then calcined at required temperature. The calcined powder was then grinded, pressed into pellet and sintered at required temperature. The final form of the sample was obtained after several intermediate grinding, formation of pellet and sintering. Similarly, La_2O_3 (99.9%) and Co_3O_4 (99.9%) were taken for preparing $LaCoO_3$ and La_2O_3 (99.9%) and NiO (99.9%) were taken for preparing $LaNiO_3$ and the same process was repeated. In Table 1, different preparation conditions are mentioned. The samples were

Table 1. Different preparation conditions

Sample	Calcination temperature	Sintering temperature	Period of sintering	No. of intermediate grinding and sintering
$LaMnO_3$	1000°C	1400°C	24 hrs	Two
$LaCoO_3$	700°C	1000°C	48 hrs	Three
$LaNiO_3$	700°C	800°C	24 hrs	One

finally well oxygenated at required oxygen pressure and temperature. X-ray diffraction analysis of the samples with CuK_α radiation showed that most of the peaks can be ascribed to the single phase cubic perovskite structure with a little trace of impurity phases which can be neglected. The compositions of the samples were confirmed by EDX analysis. The oxygen stoichiometry of the samples was determined by iodometric titration method described elsewhere [12]. They are nearly 3.20, 3.15 and 3.25 for $LaMnO_{3+\delta}$, $LaCoO_{3+\delta}$ and $LaNiO_{3+\delta}$ respectively. The electrical resistivity of the samples was measured in the standard dc four probe method in a pumped He^4 cryostat in the temperature range 1.8 K–

300 K using the CGR sensor. Magnetoresistance was measured with a Nb–Ti superconducting magnet in the field range 0–8 Tesla. The electrical contacts were made with silver paste.

3. Results and discussion

The electrical resistivity of $LaMnO_{3+\delta}$ in absence of magnetic field and in presence of two magnetic fields is shown in Figure 1. All the three curves showed that in the temperature range of 1.8 K to 30 K, the resistivity decreases with increase in temperature and then increases with increase of temperature showing a minimum at 30 K. Such a small decrease

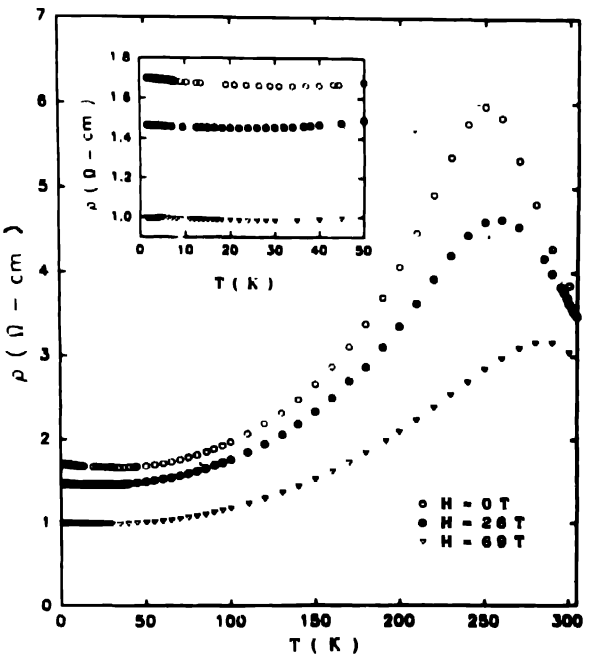

Figure 1. The resistivity *vs* temperature plot of the sample $LaMnO_{3.20}$ in absence of magnetic field and in presence of two magnetic fields. The inset shows the small increase in the resistivity at the lower temperature range.

in resistivity with increase of temperature is due to some disorder in the sample which produces quantum interference effect [14]. Above 30 K, there is a metallic behaviour which remains upto 250 K for zero field. This region can be attributed to the ferromagnetic ordering of the Mn-spins. This can be understood with the help of the double exchange model first proposed by Zener [13]. With the incorporation of the extra oxygen in the perovskite structures, a corresponding number of formerly Mn^{3+} has become Mn^{4+} and the displacement of these holes increases the conductivity and at the same time provide the mechanism for ferromagnetic interaction. In pure $LaMnO_3$, no electron transfer was possible between two Mn ions but with the introduction of some Mn^{4+} ions, a bond between

Mn^{3+} and Mn^{4+} is possible through oxygen (Mn^{3+}–O^{2-}–Mn^{4+}). At 250 K, for zero field curve, a peak in the resistivity curve occurs and the resistivity thereafter, decreases with increase in temperature. The temperature 250 K actually implicates the ferromagnetic transition temperature T_c [14,15] which is also the temperature for metal-insulator transition. With the application of magnetic field, the resistivity decreases *i.e.* a large negative magnetoresistance occurs and at T = 250 K, it shows a maximum of –55% for applied magnetic field H = 6.9 Tesla. The magnetic field also causes a shift in the peak of the resistivity curve and it is 260 K at 2.6 T and 282 K at 6.9 T and this nature has already been observed by various workers [14,16].

The magnetoresistance at low temperature as shown in Figure 2, is also high and negative. At low field, say 1T, it decreases rapidly and then the rate falls off with the increase in magnetic field. This behaviour can be explained based on double exchange between pairs of Mn^{3+} and Mn^{4+} ions. In this model, a parallel alignment of the manganese

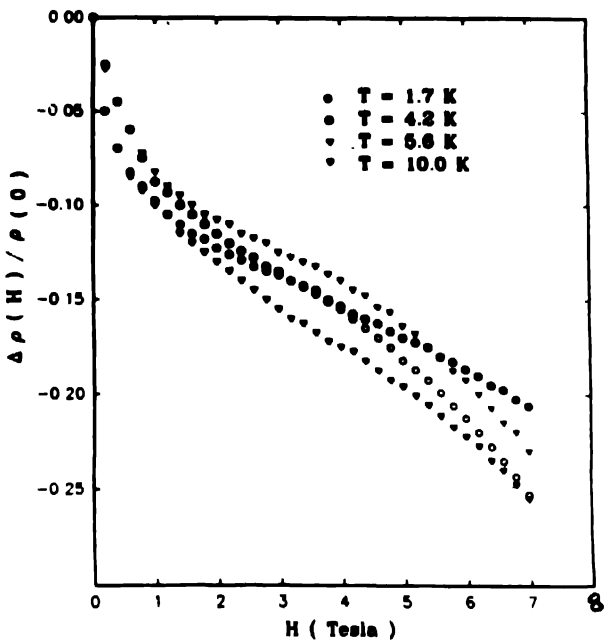

Figure 2. The magnetoresistance *vs* ferromagnetically field plot for the sample $LaMnO_{3.20}$ at four fixed temperatures

spin is required before electron can be transferred between the ions to give the electrical conductivity. At low temperature below T_c, manganese ions are ferromagnetically ordered and electron transfer between pairs of Mn^{3+} and Mn^{4+} ions inside a single domain is easy. However for an unmagnetised sample, there are many domains with different magnetisation direction. Near the domain-wall boundaries the pairs of spin of Mn^{3+} and Mn^{4+} may not be parallel. As a result, the electron transfer between pairs of Mn^{3+} and Mn^{4+} ions across the domain wall is difficult and the resistivity is high. With the application of magnetic field,

the magnetic domains tend to align along the field direction and the electron transfer across the domain wall boundaries become more easy, causing a rapid decrease in the resistivity for the application of lower magnetic field. The high field ($H > 1$T) magnetoresistance may have its origin in a small canting of the manganese moments inside each domains. With further increase in magnetic field, the canting angle will become smaller and the electron transfer between pairs of Mn^{3+} and Mn^{4+} will become easier. As a result the resistivity decreases further, giving rise to a negative magnetoresistance [17]. At 4.2 K the magnetoresistance is –25%.

The resistivity curve for the $LaCoO_{3+\delta}$ sample is shown in the Figure 3. The resistivity is almost constant at low temperature upto 47 K. Above that temperature, a sharp

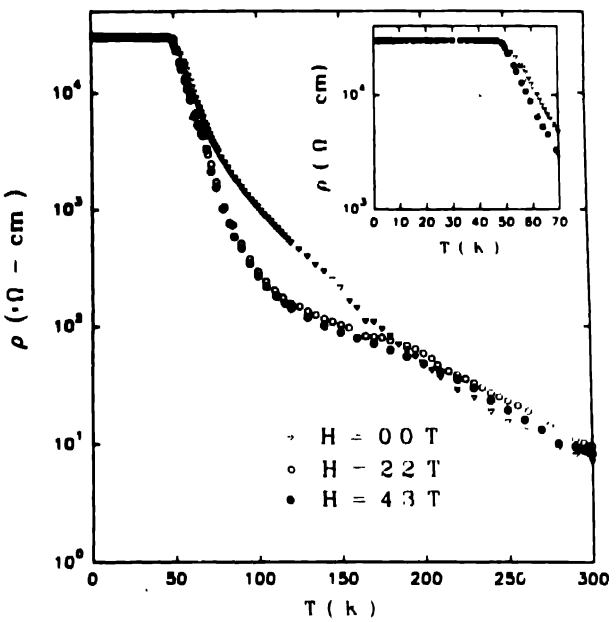

Figure 3. The resistivity *vs* temperature plot for the sample $LaCoO_{3.15}$ in absence of magnetic field and in presence of two magnetic fields. The inset shows the sharp fall in resistivity at the lower temperature range.

change in the resistivity occurs and it is of the order of 10^2 for a change in temperature of 20 K. After that the resistivity decreases in a slower rate. Application of magnetic field changes the transition temperature to a small extent. For H = 2.2 T, it is nearly 50 K and at H = 4.3 T, it is nearly 52 K. The magnetic field also affects the temperature region between 50 K to 150 K and it decreases the resistivity with its own increase. Resistivity at very low temperature range does not affect much with magnetic field. However, a positive magnetoresistance has been observed above 175 K. Such a positive magnetoresistance at high temperature, has also been observed in some La–Y–Ca–Mn–O compound [18] but the origin of this phenomena is yet to be understood. At very low temperature like 1.8 K, the sample shows a moderate positive

magnetoresistance but with the increase in temperature no significant increase of the magnetoresistance was observed.

The $LaNiO_{3+\delta}$ sample shows a resistivity behaviour which is different from the pure $LaNiO_3$ in the temperature range 1.8 K to 135 K. In this region, the resistivity shows a minimum. Above 135 K, it shows metallic behaviour. This metallic to semiconductor type of transition was not observed in pure $LaNiO_3$. A possible explanation of this nature can be given in terms of the presence of extra oxygen δ. It has already been shown that even pure $LaNiO_3$ has sufficient disorder which increases the resistivity of the sample and it has been explained by electron-electron interaction [19]. In our case also, as shown in the inset of Figure 4, the low temperature resistivity fits well with $\rho = \rho_0 - AT^{1/2}$.

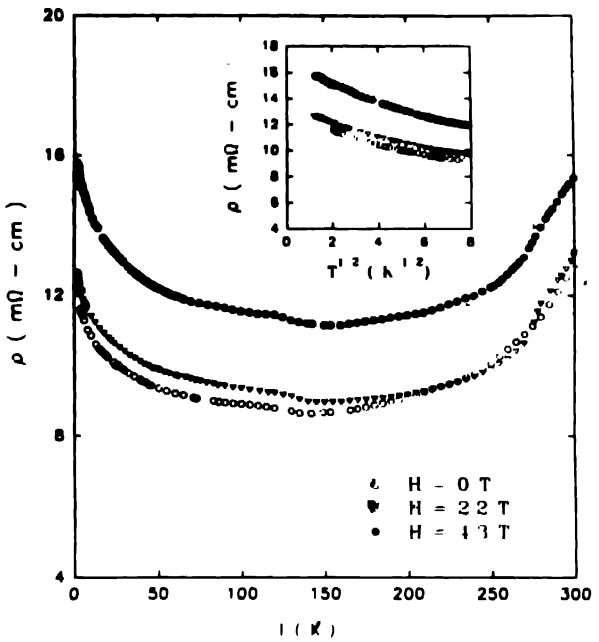

Figure 4. The resistivity *vs* temperature plot for the sample $LaNiO_{3.25}$ in absence of magnetic field and in presence of two magnetic fields. The inset shows the resistivity *vs* $T^{1/2}$ plot at lower temperature region.

With the application of the magnetic field, the resistivity increases and also the transition temperature shifts towards the higher temperature. For $H = 2.2$ T, it is nearly 145 K and for $H = 4.3$ T, it is 150 K. Between 150 K and 250 K, the resistivity gives T^2 dependence and above 250 K, resistivity is linear with T.

The large negative magnetoresistance in $LaMnO_{3+\delta}$ system has been qualitatively explained by the double exchange mechanism. The semiconductor behaviour of $LaCoO_{3+\delta}$ can be interpreted in terms of the combined effects of the temperature dependent spin state transition from low spin state to high spin state of Co ion and the thermal activation characterised by the conventional semiconductors [20]. In $LaNiO_{3+\delta}$, the increase in

resistivity at low temperature is due to electron-electron interaction and the metallic part is governed by the electron-phonon scattering as in the usual metals.

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